

Hot-Gas Desulfurization with Sulfur Recovery

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Introduction

At its Piñon Pine Power project, Sierra Pacific Power Company is beginning to operate an advanced integrated gasification combined cycle (IGCC) power systems. Coal is gasified in a fluidized-bed of limestone which maintains the level of hydrogen sulfide (H₂S) in the raw coal gas at several hundred parts per million. In an external desulfurizer, H₂S is further reduced to low parts per million levels using regenerable zinc-based sorbents. During regeneration of the sulfided sorbent, there is an opportunity to produce elemental sulfur which is a valuable by-product, an essential industrial commodity, that can be easily stored, transported, and sold. Currently, the leading technologies for hot-gas desulfurization (HGD) use air- or dilute-air-regeneration of the sorbents (Piñon Pine uses air) to produce a tail gas containing mostly nitrogen plus sulfur dioxide (SO₂). Catalytic reduction of the SO₂ to elemental sulfur with a coal gas slip-stream using the Direct Sulfur Recovery process (DSRP) is a leading first generation technology to produce elemental sulfur.

The Federal Energy Technology Center (FETC) is sponsoring the development of the DSRP (Dorchak et al., 1991; Portzer and Gangwal, 1995), a single-step catalytic process that uses the reducing components (H₂ and CO) of coal gas to directly and efficiently reduce the SO₂ to elemental sulfur:



In the DSRP, for every mole of SO₂, two moles of reducing gas are used, leading to a small but noticeable consumption of coal gas. Although the DSRP continues to show promise and has undergone field testing at gasifier sites (Portzer et al., 1996), alternative or improved processing is still possible.

Objective

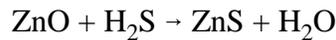
The objective of this study is to develop a second generation HGD process that regenerates the sulfided sorbent directly to elemental sulfur using SO₂, with minimal consumption of coal gas. The goal is to have better overall economics than DSRP when integrated with the overall IGCC system.

Approach

After evaluating several alternatives, direct production of elemental sulfur during sorbent regeneration using SO_2 as an oxidizing agent was chosen as the approach for development of the second generation HGD process (Gangwal et al., 1995, 1996). SO_2 -regeneration involves the reaction of nearly pure SO_2 with sulfided sorbent at elevated temperature and pressure. Under these conditions, elemental sulfur is the only product predicted from thermodynamics. The Research Triangle Institute (RTI) has conceptualized a process that comprises desulfurization (sulfidation of the sorbent) and sequential SO_2 -regeneration and SO_2/O_2 -regeneration that is referred to as the Advanced Hot Gas Process (AHGP) (Figure 1). In the AHGP, a modified zinc-iron sorbent is used so that regeneration to elemental sulfur can be accomplished using SO_2 and O_2 without the need for a coal gas slipstream as a reductant. The zinc component in the sorbent provides the SO_2 required to regenerate the iron component.

The key chemical reactions of interest are as follows:

1. Sulfidation (Desulfurization Reactor)



2. SO_2 regeneration (Regenerator– Stage 1)

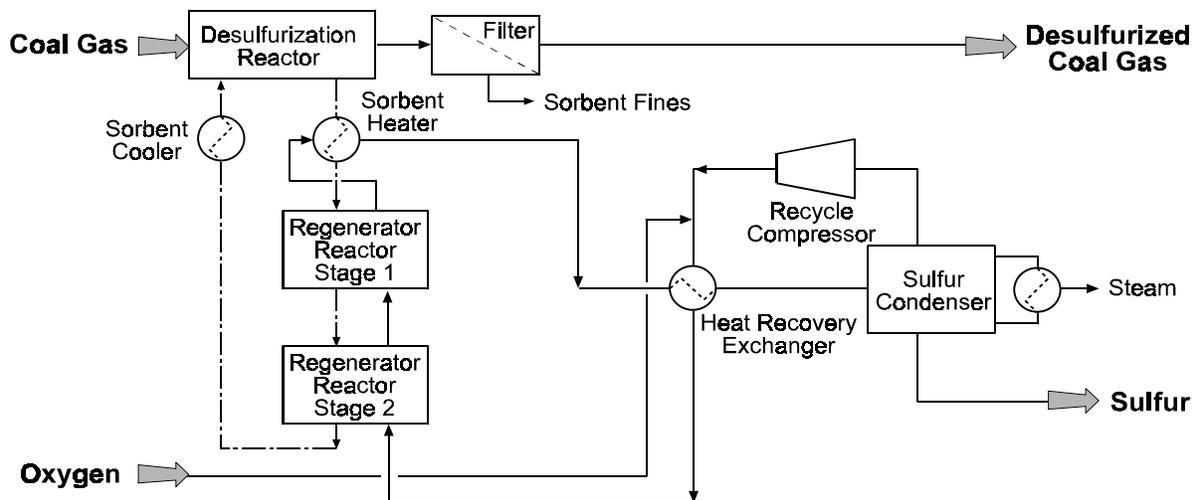
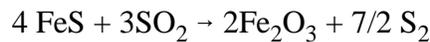
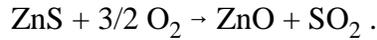
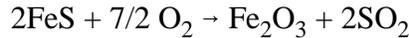


Figure 1. Advanced hot-gas process (AHGP).

3. O₂ regeneration (Regenerator – Stage 2)



The AHGP conceptualization was refined following successful bench-scale testing of several sorbent formulations, and long duration testing of one highly attrition-resistant formulation in a fluidized-bed reactor (Portzer et al., 1997). As the process is currently conceived, the desulfurization of the coal gas (sulfidation of the sorbent) takes place at about 450 °C at the pressure of the coal gas (typically 20 atm) in the desulfurization reactor. The sulfided sorbent enters a multistage reaction vessel to be heated to 600 °C using waste heat from the regenerated sorbent. The heated sorbent passes to Stage 1 of the regenerator to contact the recirculating SO₂ gas stream. The elemental sulfur formed exits in the gaseous state. The partially regenerated sorbent then passes into Stage 2 of the regenerator where oxygen will be added to the regeneration gas. In this heat-integrated process, the energy from the exothermic O₂ regeneration is used to drive the endothermic SO₂ regeneration. The regenerated sorbent is then cooled and recirculated to the desulfurization reactor.

The recirculation loop for the regeneration gas functions as follows: the regeneration off-gas exiting from Stage 1 is cooled to condense out the sulfur, which is removed as a molten product. The exit gas from the sulfur condenser is then compressed slightly (to recover the pressure drop losses from recirculation) and is reheated by countercurrent exchange with the hot regeneration off-gas. With control of the ratio of iron and zinc in the sorbent, and by balancing the amount of oxygen supplied to Stage 2 with the amount of elemental sulfur that is actually being produced, the SO₂ material balance of the recirculation loop can be maintained. For startup purposes, an external supply of liquid SO₂ could be used to charge the recirculation loop.

RTI subcontracted with North Carolina State University (NCSU) to prepare an engineering evaluation of the AHGP compared to a system that uses DSRP to produce an elemental sulfur product (Gangwal et al., 1998). Material and energy balances were prepared using the ASPEN PLUS™ process simulation software. Reactor sizing was based on general fluidized-bed and transport reactor design concepts; costing followed open literature published guidelines.

Project Description

The first phase of the NCSU work was generation of process simulations (with complete mass and energy balances) of the two comparison processes in order to establish process stream conditions and flow rates. The stream data were then used in the second phase of the work to calculate equipment sizes and estimate capital and operating costs of each process.

The nominal plant size of 260 MWe (net) was chosen as the design basis for the process simulations that were conducted using the ASPEN PLUS™ software. Table 1 lists the flow rate, composition, and conditions of the clean coal gas exiting the simulations of both processes; the basis is an O₂-blown gasifier. The process simulation work took advantage of the large built-in physical property database in ASPEN PLUS™. The rigorous algorithms for heat capacities, heats

of reaction, reaction equilibria based on Gibbs free energy minimization, and vapor-liquid equilibrium data based on Peng-Robinson equation-of-state resulted in accurate accounting of the heat effects and phase changes. Selection of appropriate “tear” streams and convergence criteria resulted in consistently converged material and energy balances for a given set of conditions.

For both processes the scope of the equipment and process steps included in the simulations were the same: coal gas desulfurization (but not the high-temperature particulate removal), regeneration of the desulfurizing sorbent, and production, isolation, and short-term storage of elemental sulfur. Figure 2 presents the comparison HGD process based on using DSRP to produce elemental sulfur. The desulfurization takes place at about 600 °C and at the pressure of the coal gas (20 atm). The sulfided sorbent passes to the regenerator where it is contacted with preheated, compressed air. The regeneration off-gas (ROG), containing approximately 14 vol% SO₂, is the feed to the DSRP reactor. In this reactor, the ROG is contacted with a slipstream of the coal gas to produce a gas stream containing mostly nitrogen plus elemental sulfur. The DSRP reactor effluent is then cooled to recover the sensible heat, and the sulfur is condensed while producing low-pressure steam. The gas stream from the condenser, the DSRP tail gas, contains some sulfur compounds (H₂S and SO₂). In order to eliminate a potential emission stream in this process conceptualization, the tail gas is recompressed slightly and recycled to the desulfurizer.

Table 1. Clean Coal Gas

Composition (vol%)	
H ₂	27
CO	35.5
CO ₂	12.5
H ₂ O	19
N ₂	6
H ₂ S	20 ppm
Flow rate (lb/h)	450,000
Pressure (psia)	275
Temperature (°C)	460

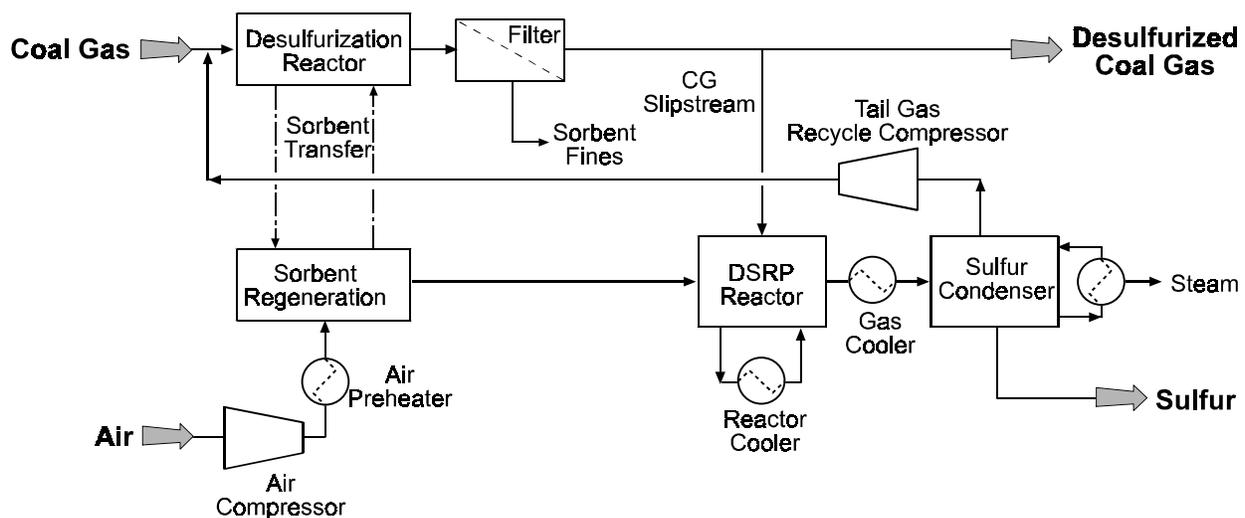


Figure 2. Hot-gas desulfurization with DSRP.

Base case simulations of both processes assumed 0.85 mol% H₂S in the coal-gas feed. Such an H₂S concentration in the coal gas would be produced by an oxygen-blown Texaco gasification using a roughly 3.6 wt% sulfur-containing coal. Both base cases generate 260 MWe from the clean coal gas. Alternative cases were considered that varied sulfur content of the coal gas, and overall plant size. Table 2 lists the conditions in alternative cases, following the nomenclature that NCSU used. In all cases, a coal-gas feed pressure and temperature of 275 psia and 482 °C, respectively, was used. Table 3 shows the composition and flow rate of the raw coal gas feed to the base case HGD processes. The requirement of a higher amount of coal gas to produce the same 260 MW power by DSRP versus the AHGP is noteworthy.

In order to conduct the second phase of the engineering comparison, and make preliminary cost estimates for the two processes, conceptual equipment designs were required. The focus of this effort was on the reactor designs.

In the case of the AHGP, there is a need to transfer the sorbent from the desulfurization reactor to the multistage regenerator, and there are sorbent heat transfer requirements; fluidized-bed reactors were envisioned. Figure 3 shows the concept of the reactor configuration used for the simulation—a transport desulfurizer and a multistage bubbling fluidized-bed regenerator. The regenerator vessel combines two stages of regeneration with one stage of heat transfer (to recover a portion of the heat of reaction as preheat for the sorbent). A large cross-sectional area reactor was required to provide a sufficient residence time for the slow SO₂ regeneration stage.

Establishing the rigorous process simulation showed that the recirculation rate of the SO₂ stream is set by the gas velocity needed in the regeneration reactors for proper fluidization of the sorbent. However, the production rate of sulfur is a function of the sorbent circulation rate and is thus somewhat independent of the regeneration gas flow rate. It should be noted that the concentration of the elemental sulfur in the regeneration loop is dependent on the engineering

Table 2. Simulation Cases Considered

Simulations	H₂S feed concentration (mol%)	MW produced
DSRP, AHGP (base cases)	0.85	260
DSRP-b, AHGP-b	2.50	260
DSRP-c, AHGP-c	0.25	260
DSRP-100, AHGP-100	0.85	110
DSRP-500, AHGP-500	0.85	540

Table 3. Raw Gas Feed to Base Case Simulations

Component	DSRP (lb/h)	AHGP (lb/h)
H ₂ S	6,300	6,100
H ₂ O	70,500	69,000
H ₂	11,800	11,500
CO	218,200	213,400
CO ₂	117,400	114,800
N ₂	36,300	35,500

design of the system; it is not just inherent to the chemistry of the regeneration process. Figure 4 is a flow diagram of a typical ASPEN PLUS™ simulation of the AHGP showing how multiple simulation blocks were used to simulate the reactor system.

The DSRP-based process was assumed to use a dual transport reactor configuration for desulfurization and sorbent regeneration of the same design this is used for the external desulfurizer at the Sierra Pacific Power Piñon Pine plant (Figure 5). Using “neat air” regeneration, the regeneration off-gas (“tail gas” on the figure) would contain 14% SO₂. For the DSRP reactor itself, a fast fluidized bed with an alumina-based catalyst was conceptualized, as Figure 6 shows. The heat of reaction is removed, and medium pressure steam generated, by

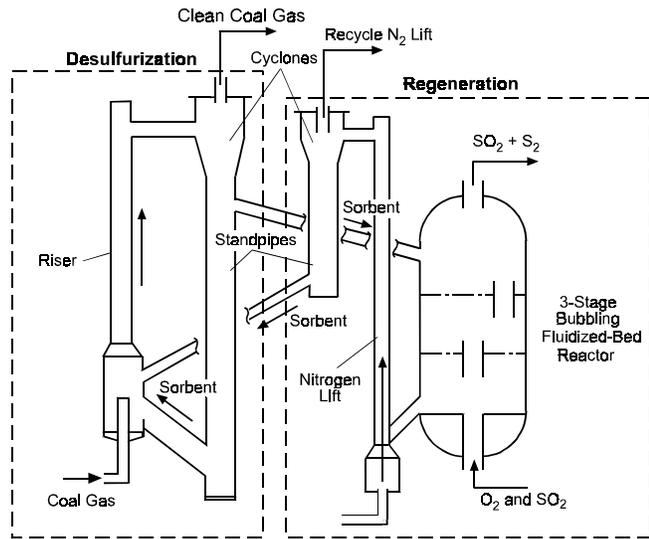


Figure 3. Schematic of AHGP desulfurization and regeneration reactors.

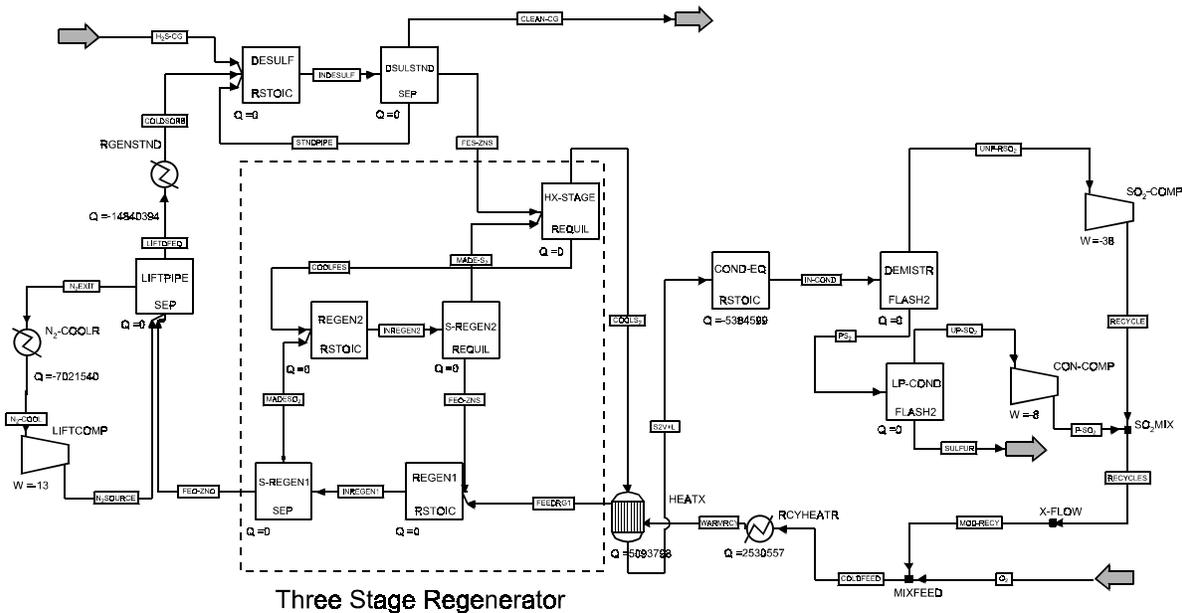


Figure 4. Flow diagram of a typical ASPEN PLUS simulation of the AHGP.

circulating the sorbent through an external heat exchanger.

Results/Accomplishments

For the economic analysis, the recovered sulfur was assumed to have a market value, and thus generate a cost credit. Coal gas consumed in the process was evaluated at a cost based on the potential power generation that was lost. High-pressure steam generated in the process was assumed to provide a cost credit based on the power that could be recovered from it.

The preliminary process and economic evaluations conducted using ASPEN PLUS are summarized in Figure 7, which compares key elements using a simple method where each parameter for the DSRP-based process is arbitrarily assigned the value of 1.0. A range of values is produced for AHGP to cover the various cases being considered. The big advantage of the AHGP is clearly the reduced parasitic consumption of coal gas. The other operating cost elements are also lower for AHGP because that process has a considerably lower compression power requirement. A desulfurization process based on the DSRP requires a large flow of compressed air to provide the oxygen necessary to regenerate the sulfided sorbent and thus has a large compressor horsepower duty. By comparison, the AHGP uses oxygen only for a smaller, polishing regeneration and, by using pure oxygen, the compression duty is lowered further. The AHGP also has the SO₂ loop recycle compressor, but its duty is quite small compared to the DSRP air compressor.

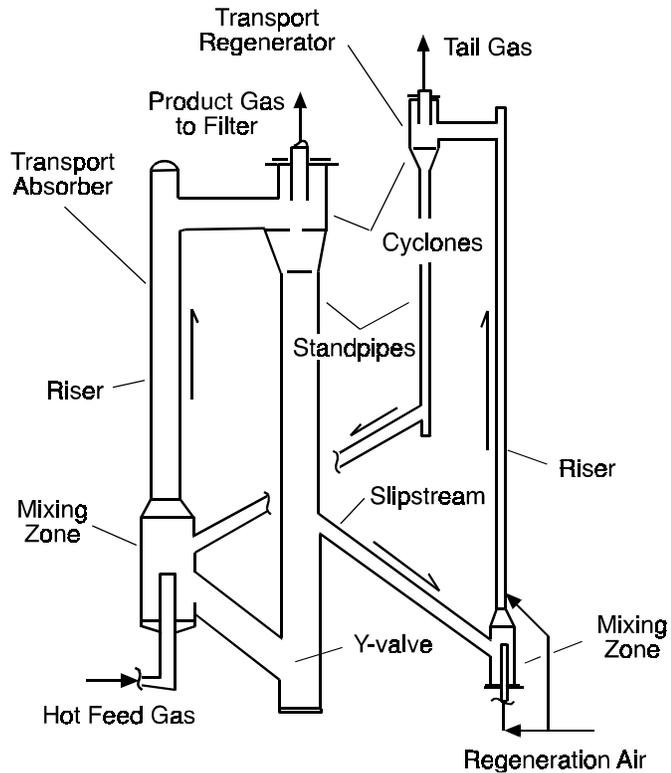


Figure 5. Schematic of Sierra Pacific external desulfurization system.

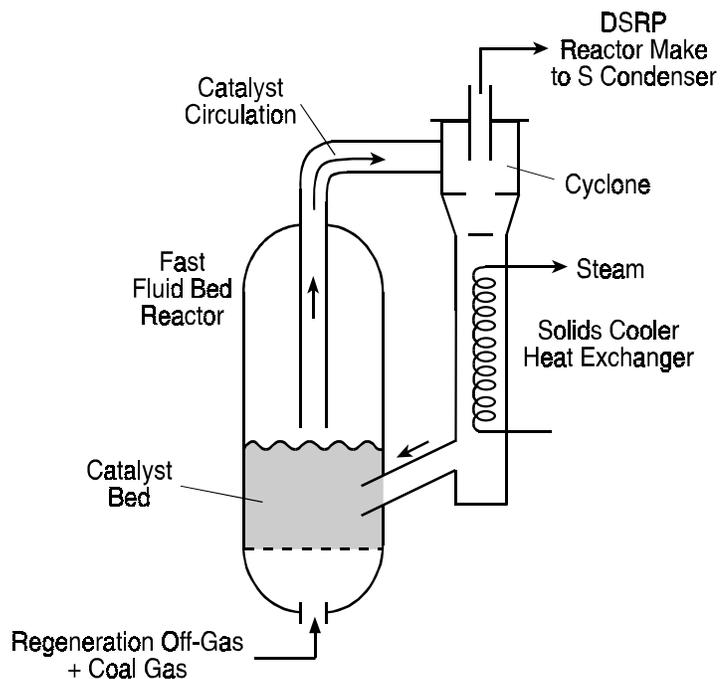


Figure 6. Fast fluidized-bed DSRP reactor.

The value of “capital cost of all equipment” for the AHGP is higher than for the DSRP-based process, as Figure 5 shows. The higher equipment cost is primarily due to the higher cost of the AHGP reactor vessel(s). Although there are three separate reactor steps required with the DSRP-based process, the single AHGP multi-stage regeneration reactor vessel(s) is larger. The larger size is primarily due to the longer residence time required for the SO₂ regeneration.

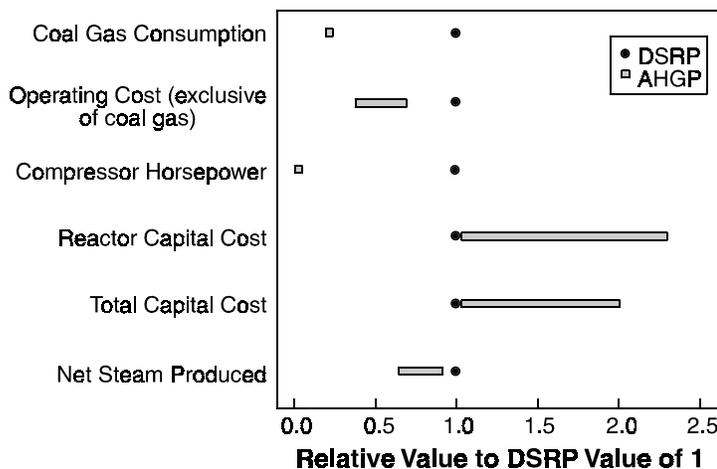


Figure 7. Comparison of key elements of DSRP and AHGP.

Another advantage of the DSRP is that it lacks the large recirculating process stream, and therefore would be the easier process to operate. It is anticipated that balancing the SO₂ production and consumption in the AHGP to maintain the SO₂ recirculation may be difficult. Presumably a simpler process would have lower operating labor costs.

Although the AHGP has a higher initial cost, indicated by its larger capital requirements, it has a significantly lower annual operating cost than DSRP. As Figure 8 shows, the operating cost advantage of the AHGP increases as the amount of sulfur to be recovered increases. The negative annual costs of AHGP at higher sulfur feed result from the sulfur credit with less consumption of coal gas. The operating cost difference is large enough to offset the installation cost of AHGP. As Figure 9 shows, AHGP has a lower cumulative HGD investment after only 2 years of operation. Both Figures 8 and 9 are presented to illustrate only cost comparison of the two processes. Emphasis should not be placed on the accuracy of the absolute cost numbers presented in these figures.

Application/Benefits

ASPEN simulations of DSRP and AHGP revealed the complexity of both HGD processes. The AHGP appears to be the more difficult process to operate and may require more employees than the DSRP. Capital costs for the AHGP are higher than those for the DSRP—development of DSRP is also much closer to commercialization than AHGP. However, annual operating costs for the AHGP appear to be considerably less than those of the DSRP. Preliminary economic comparison shows that the total cost (capital plus cumulative operating cost) of implementing AHGP will be less than that of implementing DSRP after as little as 2 years of operation. Thus, despite its greater complexity, the potential savings with the AHGP encourage further development and scaleup of this advanced process.

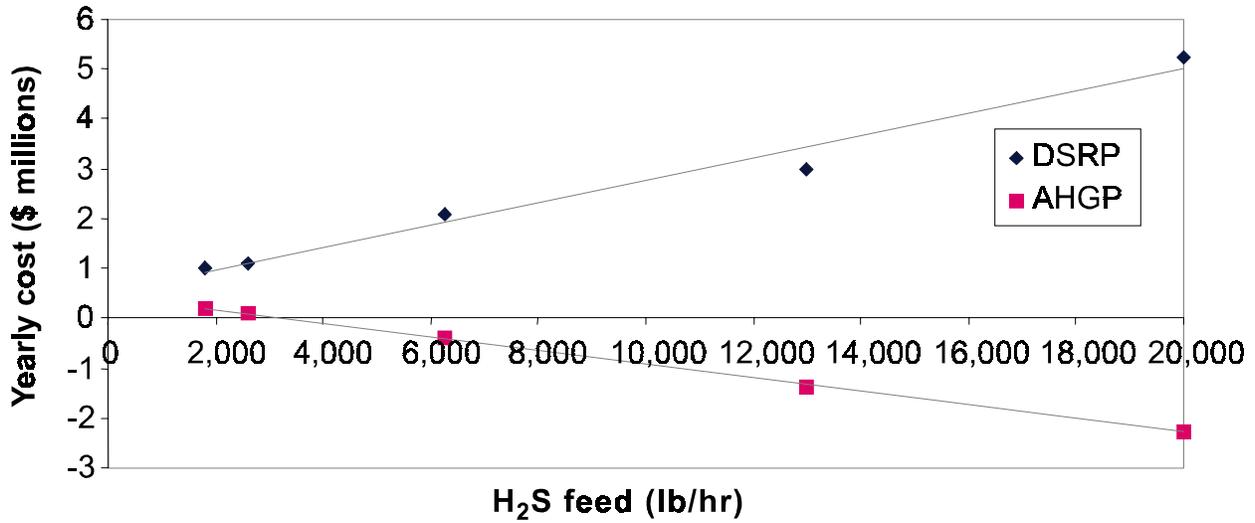


Figure 8. Annual costs as a function of sulfur feed.

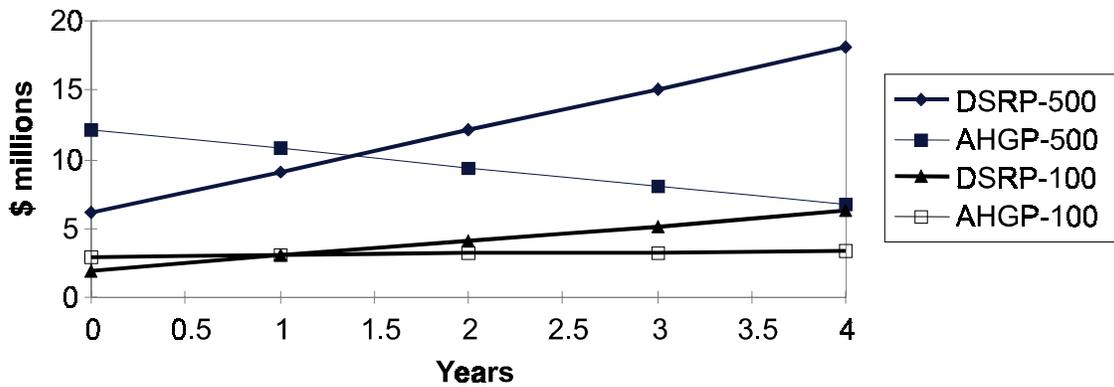


Figure 9. Cumulative HGD investment.

Future Activities

Additional sorbent modification and testing to demonstrate H₂S control to under 20 ppmv in the AHGP is planned for FY98-99. Bench-scale testing with actual coal gas using the RTI/FETC Mobile Laboratory at the Power Systems Development Facility (PSDF) is planned for the 1999-2000 time frame. This latter activity is in conjunction with a planned field test of the DSRP (Contract No. DE-93-AC21-93MC30010) and is described in more detail in another paper in these Proceedings, titled *Bench-Scale Demonstration of Hot-Gas Desulfurization Technologies*.

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